

PATENT ABSTRACTS OF JAPAN

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(54) MOISTURE CURING TYPE BINDER FOR PAVEMENT

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a moisture curing type binder excellent in flexibility and weather resistance, low in cost and extremely improved in workability, by using a mixture of a specific aliphatic isocyanate prepolymer.
SOLUTION: This moisture curing type binder for pavement comprises (A) 100 pts.wt. of a terminal NCO group-containing urethane prepolymer obtained by reacting an alicyclic polyisocyanate such as isophorone diisocyanate with a polyol [preferably a polyol containing at least ≥ 50 wt.% of one selected from a polytetramethylene ether glycol having 500-6,000 molecular weight and a polyoxypropylene polyol] and (B) 10-100 pts.wt., preferably 20-75 pts.wt. of an isocyanurate ring-containing hexamethylene diisocyanate-based prepolymer and has preferably $\geq 65\%$ solid content and $\leq 20,000$ mpas/ 25° C viscosity.

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3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is easy to construct and relates to the moisture curing type binding material for pavement excellent in weatherability etc.

[0002]

[Description of the Prior Art]In order to return storm sewage in the earth on a motor pool, a foot walk, etc. in recent years, water penetration asphalt concrete and water penetration cement concrete are used increasingly. After forming the foundation layer which consists of water penetration asphalt concrete or water penetration cement concrete on a railroad bed, Aggregate, such as a living rock and ceramics, is prepared with urethane resin or an epoxy resin in a construction site, The method of covering with and stiffening with a rake, a trowel, etc. and finishing, the method of finishing by the interlocking block which made the concrete block surface harden aggregate, such as a living rock and ceramics, with an epoxy resin etc., The method of covering with and making FRP and a metal mold to the Plastic solid which stiffened aggregate, such as a living rock and ceramics, etc. are performed.

[0003]

[Problem(s) to be Solved by the Invention]However, by an outdoor exposure, an epoxy resin produces discoloration, chalking, etc. and is inferior to endurance or design nature. In order to consider it as high intensity, the urethane resin binding material which uses isocyanates, such as tolylene diisocyanate, turns yellow, and does not have design nature. for this reason, JP,6-234963,A and JP,6-172484,A --- like ---less --- yellowing, although using the isocyanate of a type is proposed, Become hyperviscosity, in order that JP,6-234963,A may use PPG of low molecular weight, workability is bad and JP,6-172484,A carries out copolymerization of the isocyanate to an acrylic resin, but. Since the reaction of the isocyanate to be used is slow, there are problems, such as becoming the things and high cost which need a lot of catalysts. Although urethane resin of non-yellow transformation may be used as topcoat these days, there are also many problems --- there is the necessity that the process of construction increases and carries out a spray.

[0004]

[Means for Solving the Problem]In order that this invention persons may solve an aforementioned problem, when examination is repeated variously, by using a mixture of a specific aliphatic series isocyanate prepolymer, It excelled in flexibility or weatherability, the knowledge of a very good moisture curing type binding material for pavement of workability being obtained by low cost was carried out, it inquired further wholeheartedly, and this invention was completed. Namely, end NCO group content urethane prepolymer (A) 100 weight section produced by this invention making polyol react to (1) alicyclic polyisocyanate, A moisture curing type binding material for pavement which carries out 10-100 weight-section content of the hexamethylene di-isocyanate system prepolymer (B) which has an isocyanurate ring, (2) Solid content is 65 % of the weight or more, and viscosity. A moisture curing type binding material for pavement of the aforementioned (1) statement which is less than 20,000 mpas/25 **, (3) Polyol is a molecular weight. Polytetramethylene ether glycol of 500-6000, At least one sort chosen from polyoxypropylene polyol A moisture curing type binding material for pavement of the aforementioned (1) statement which is what is contained 50% of the weight or more, and moisture curing type binding material for pavement given in (4) aforementioned (1) a paving material which contains 3 to 40 % of the weight, and an unguent 97 to 50% of the weight --- it comes out.

[0005]

[Embodiment of the Invention]As an alicyclic isocyanate used for this invention, For example, the compound which 2-5 isocyanate groups [2-3] combined with cyclohexane rings, such as isophorone diisocyanate, hydrogenation xylylene diisocyanate, and a hydrogenation methylenebis phenylisocyanate, preferably via direct or a carbon atom is mentioned. Especially in these, since isophorone diisocyanate is excellent in reactivity, weatherability, and heat resistance, it is desirable. As polyol which can be used for this invention, for example Polyoxypropylene polyol, Polyoxypropylene ethylene polyol, polytetramethylene ether glycol, Ethylene glycol, propylene glycol, dipropylene glycol, An average functional group number with the average molecular weights 50-6,000, such as 1,4-butanediol, trimethylolpropane, polycaprolactone polyol, polyvalerolactone polyol, and polyester polyol. Although the conventionally publicly known polyol of 2-4 is mentioned, It is preferred independent or to consider it as a mixture and to contain the polyoxypropylene polyol of the molecular weights 500-6000, polyoxy ethylene propylene polyol, and polytetramethylene ether glycol 50% of the weight or more. If there is little content of the polyol of these molecular weights 500-6000, viscosity may become high, and workability may worsen.

[0006]as for a urethane prepolymer (A), the isocyanate group (NCO) of alicyclic polyisocyanate receives the active hydrogen group (OH) of polyol --- for example, a NCO/OH equivalent ratio --- 1.2-3.0 --- preferably alicyclic polyisocyanate and polyol in 1.5-2.5. It is obtained by making it react. Reaction temperature is usually about 60-100 **, and reaction time is usually about 2**10 hours. At this

[0007]By the urethane prepolymer (A) obtained by the above-mentioned reaction, as a binding material for pavement in addition, Since the workability and hardenability in the case of construction are inferior, the hexamethylene di-isocyanate system prepolymer (B) which contained the isocyanurate ring further is usually used ten to 100 weight section to (A)100 weight section, carrying out 20-75 weight-section mixing preferably. The hexamethylene di-isocyanate system prepolymer (B) having contained the isocyanurate ring is hexamethylene di-isocyanate (it may be called HDI for short.)the very thing — it can obtain by heating at 20-80 °C by making alkali salt of carboxylic acid into a catalyst, making an isocyanurate ring form as indicated to the publicly known method, for example, JP.2-42068.A, and suspending a reaction by a silicate. As the typical thing, it is general formula (I).

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{DCN}-(\text{CH}_2)_8-\text{N}-\text{C}-\text{N}-(\text{CH}_2)_8-\text{NCO} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \\ | \quad | \\ (\text{CH}_2)_8-\text{NCO} \end{array} \quad (1)$$

[0008] Additive agents, such as various coupling agents, such as a publicly known plasticizer, a defoaming agent, weatherproof stabilizer, heat-resistant stabilizer, and a silane coupling agent, may be added conventionally if needed besides the ingredient of the above (A) and (B). 65% of the weight or more, preferably, solid content is 75 % of the weight or more, and viscosity the moisture curing type binding material for pavement obtained A thing 10,000 mpas(es)/25 ** or less can use preferably 20,000 mpas/25 ** or less advantageously especially from the viewpoint of workability. Isocyanate group content in a binding material 5 to 25 % of the weight, isolation NCO monomer It is preferred from the physical-properties side of a hardened material to consider it as 2 or less % of the weight. As aggregate of nature [aggregate / which is used for this invention] for example, a pea gravel, a crushed stone, decomposed granite soil, silica sand, a piece of wood, chaff, mica, a milt balloon, a shell grinding thing, etc. are raised, and grinding things, such as ceramics, a waste roof tile, waste glass, a waste plastic, and waste rubber, are mentioned as artificial aggregate. These can be independent or can be used combining two or more sorts. the compounding ratio of the moisture curing type binding material for pavement, and aggregate — weight ratio 3**40:97-60 — it is 4-30:96-70 preferably. The charge of pavement material obtained by kneading a binding material and aggregate can obtain a permeable pavement layer by constructing and making it harden at ordinary temperature. Or the mold goods for water-permeable pavings can be obtained by paying the charge of pavement material to a mold, and making it harden with ordinary temperature or heating. Since it is a moisture curing type, it may be influenced by hardenability according to a weather condition. Therefore, the publicly known catalyst for urethane, polyol, etc. may be used as a hardening agent as occasion demands. Additive agents, such as various coupling agents, such as paints, a plasticizer, a defoaming agent, weatherproof stabilizer, heat-resistant stabilizer, and a silane coupling agent, may be mixed at this time.

[Example] Although a synthetic example, an example, and a comparative example are given to below and this invention is further explained to it, this invention is not limited at all by these. The part in a synthetic example, an example, and a comparative example expresses a weight section, and % expresses weight %.

[0010]290.1 copies of synthetic isophorone diisocyanate of the synthetic example 2 resin 2, 92.3 copies of poly(oxypropylene)triol of the molecular weight 320 (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make), 186.1 copies of polytetramethylene ether glycols (PTG-1000, the Hodogaya Chemical industry company make) and 116.5 copies of xylene of the molecular weight 1,000 were taught to the reaction apparatus, and the urethane-ized reaction was performed at 80-100 ** under the nitrogen air current for about 2 hours. Furthermore 0.07 copy of dibutyltin dilaurate was added, and the reaction was performed for 3 hours. The HDI system prepolymer which cools at 40 ** after ending reaction, and contains an isocyanurate ring (D-170 N₈ of Takenate) Takeda Chemical Industries, Ltd. — shrine 297.0 copy and 9.9 copies of silane coupling agents (SH-6040, the Toray Industries Dow Corning make) are

added, and it has an isocyanate group at the end — it was transparent and the light yellow urethane prepolymer was obtained. Viscosity 2,400 mpas/25 **, and 11.7% of an isocyanate group content separate this prepolymer. It was NCO 0.95%.

[0011] 290.1 copies of synthetic isophorone diisocyanate of the synthetic example 3 resin 3, 92.3 copies of poly(oxypropylene)triol of the molecular weight 320 (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make), 186.5 copies of poly(oxypropylene)diol (the bamboo rack P-22, the Takeda Chemical Industries [Ltd.], Ltd. make) and 116.5 copies of xylene of the molecular weight 1,000 were taught to the reaction apparatus, and the urethane-ized reaction was performed at 80–100 ** under the nitrogen air current for about 8 hours. It cools at 40 ** after ending reaction, and an isocyanurate ring is included. 297.0 copies of HDI system prepolymers (Takenate D-170N, Takeda Chemical Industries [Ltd.], Ltd. make) were added, and the light yellow urethane prepolymer was obtained by the transparency which has an isocyanate group at the end. This prepolymer was viscosity 2,530 mpas/25 **, 11.6% of an isocyanate group content, and isolation NCO 0.96%.

[0012] 124.3 copies of synthetic isophorone diisocyanate of the synthetic example 4 resin 4, 39.5 copies of poly(oxypropylene)triol of the molecular weight 320 (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make), 79.9 copies of polytetramethylene ether glycols (PTG-1000, the Hodogaya Chemical industry company make) and 50 copies of xylene of the molecular weight 1,000 are taught to a reaction apparatus, and it is abbreviation at 80–100 ** under a nitrogen air current. The urethane-ized reaction was performed for 2 hours. Furthermore 0.03 copy of dibutyltin dilaurate was added, and the reaction was performed for 3 hours. The HDI system prepolymer which cools at 40 ** after ending reaction, and contains an isocyanurate ring (D-170 Ns of Takenate) Takeda Chemical Industries, Ltd. — shrine 700 copy and three copies of silane coupling agents (SH-6040, the Toray Industries Dow Corning make) are added, and it has an isocyanate group at the end — it was transparent and the light yellow urethane prepolymer was obtained. This prepolymer was viscosity 2,860 mpas/25 **, and 16.8% of an isocyanate group content.

[0013] 414.5 copies of synthetic isophorone diisocyanate of the synthetic example 5 resin 5, 131.8 copies of poly(oxypropylene)triol of the molecular weight 320 (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make), 266.5 copies of polytetramethylene ether glycols (PTG-1000, the Hodogaya Chemical industry company make) and 166.5 copies of xylene of the molecular weight 1,000 are taught to a reaction apparatus, and it is abbreviation at 80–100 ** under a nitrogen air current. The urethane-ized reaction was performed for 8 hours. It cooled at 40 ** after ending reaction, and the light yellow urethane prepolymer was obtained by the transparency which carries out an isocyanate group owner to an end. This prepolymer was viscosity 2,730 mpas/25 **, and 7.8% of an isocyanate group content.

[0014] 485 copies of synthetic isophorone diisocyanate of the synthetic example 6 resin 6, 265 copies of poly(oxypropylene)triol (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make) of the molecular weight 320, and 250 copies of xylene are taught to a reaction apparatus. It is abbreviation at 80–100 ** under a nitrogen air current. The urethane-ized reaction was performed for 8 hours and the light yellow urethane prepolymer was obtained by the transparency which carries out an isocyanate group owner to an end. This prepolymer was viscosity 2,500 mpas/25 **, and 7.6% of an isocyanate group content.

[0015] 705.9 copies of HDI system prepolymers containing the synthetic isocyanurate ring of the synthetic example 7 resin 7 (made by Takenate D-170N Takeda Chemical Industries, Ltd., Ltd.), 52.4 copies of poly(oxypropylene)triol of the molecular weight 320 (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make), 105.9 copies of polytetramethylene ether glycols (PTG-1000, the Hodogaya Chemical industry company make) and 117.8 copies of xylene of the molecular weight 1,000 are taught to a reaction apparatus, and it is abbreviation at 80–100 ** under a nitrogen air current. The urethane-ized reaction was performed for 8 hours. It cooled at 40 ** after ending reaction, and the light yellow urethane prepolymer was obtained by the transparency which carries out an isocyanate group owner to an end. This prepolymer was viscosity 20,900 mpas/25 **, and 11.6% of an isocyanate group content.

[0016] 213.5 copies of synthetic isophorone diisocyanate of the synthetic example 8 resin 8, 67.9 copies of poly(oxypropylene)triol of the molecular weight 320 (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make), 137.2 copies of polytetramethylene ether glycols (PTG-1000, the Hodogaya Chemical industry company make) and 350 copies of xylene of the molecular weight 1,000 are taught to a reaction apparatus, and it is abbreviation at 80–100 ** under a nitrogen air current. The urethane-ized reaction was performed for 2 hours. Furthermore 0.05 copy of dibutyltin dilaurate is added, and it is abbreviation. The reaction was performed for 3 hours. It cooled at 40 ** after ending reaction, 7.3 copies of silane coupling agents (made by SH-6040 Toray Industries Dow Corning) were added, and the light yellow urethane prepolymer was obtained by the transparency which carries out an isocyanate group owner to an end. This prepolymer was viscosity 80 mpas/25 **, and 8.6% of an isocyanate group content.

[0017] 380 copies of synthetic hexamethylene diisocyanate of the synthetic example 9 resin 9, 159.7 copies of poly(oxypropylene)triol of the molecular weight 320 (the act call G-530, the Takeda Chemical Industries [Ltd.], Ltd. make), 322.8 copies of polytetramethylene ether glycols (PTG-1000, the Hodogaya Chemical industry company make) and 119.4 copies of xylene of the molecular weight 1,000 were taught to the reaction apparatus, and the urethane-ized reaction was performed at 80–100 ** under the nitrogen air current for about 2 hours. Furthermore 0.09 copy of dibutyltin dilaurate was added, and the reaction was performed for about 3 hours. It cooled at 40 ** after ending reaction, 8.6 copies of silane coupling agents (made by SH-6040 Toray Industries Dow Corning) were added, and the light yellow urethane prepolymer was obtained by the transparency which carries out an isocyanate group owner to an end. This prepolymer was viscosity 2,400 mpas/25 **, and 9.6% of an isocyanate group content.

[0018] Resin 1 obtained in 1,000 copies of example 1 living rocks (particle diameter 5 mm), and the synthetic example 1 70 copies and 0.35 copy of hardening accelerator (formate S-9 Takeda Chemical Industries [Ltd.], Ltd. make) were mixed, it puts into a mold, it was stiffened, and 40 mm long, 160 mm wide, and a 40-mm-thick Plastic solid were created. 23 ** and 50%RH estimated physical properties for this after care of health for seven days. The result It is shown in [Table 1].

Resin 2 obtained in 1,000 copies of example 2 living rocks (particle diameter 5 mm), and the synthetic example 2 70 copies and 0.35 copy of hardening accelerator (formate S-9 Takeda Chemical Industries [Ltd.], Ltd. make) were mixed, it puts into a mold, it was stiffened, and 40 mm long, 160 mm wide, and a 40-mm-thick Plastic solid were created. 23 ** and 50%RH estimated physical properties for this after care of health for seven days. The result It is shown in [Table 1].

Resin 3 obtained in 1,000 copies of example 3 living rocks (particle diameter 5 mm), and the synthetic example 3 70 copies were mixed, it puts into a mold, it was stiffened, and 40 mm long, 160 mm wide, and a 40-mm-thick Plastic solid were created. 23 ** and 50%RH estimated physical properties for this after care of health for seven days. The result It is shown in [Table 1].

[0019]Resin 4 or 5 obtained in the comparative example 1 and 1,000 copies of two living rocks (particle diameter 5 mm), and the synthetic examples 4 and 5 70 copies and 0.35 copy of hardening accelerator (formate S-9 Takeda Chemical Industries [, Ltd.], Ltd. make) were mixed, it puts into a mold, it was stiffened, and 40 mm long, 160 mm wide, and a 40-mm-thick Plastic solid were created. 23 ** and 50%RH estimated physical properties for this after care of health for seven days. The result It is shown in [Table 2].

Resin 6 or 7 obtained in the comparative example 3 and 1,000 copies of four living rocks (particle diameter 5 mm), and the synthetic examples 6 and 7 70 copies were mixed, it puts into a mold, it was stiffened, and 40 mm long, 160 mm wide, and a 40-mm-thick Plastic solid were created. 23 ** and 50%RH estimated physical properties for this after care of health for seven days. The result It is shown in [Table 2].

[0020]Resin 8 or 9 obtained in the comparative example 5 and 1,000 copies of six living rocks (particle diameter 5 mm), and the synthetic examples 8 and 9 70 copies and 0.35 copy of hardening accelerator (formate S-9 Takeda Chemical Industries [, Ltd.], Ltd. make) were mixed, it puts into a mold, it was stiffened, and 40 mm long, 160 mm wide, and a 40-mm-thick Plastic solid were created. 23 ** and 50%RH estimated physical properties for this after care of health for seven days. The result It is shown in [Table 2].

the epoxy resin (TEKUEPO floor line-150R.) of 1,000 copies of comparative example 7 living rocks (particle diameter 5 mm), and 2 liquid reaction type Takeda Chemical Industries, Ltd. — it obtained the shrine 52.5 copy and one sort of epoxy resins [17.5 copies of] (TEKUEPO floor line-150R, Takeda Chemical Industries [, Ltd.], Ltd. make) were mixed, it puts into a mold, it was stiffened, and 40 mm long, 160 mm wide, and a 40-mm-thick Plastic solid were created. 23 ** and 50%RH estimated physical properties for this after care of health for seven days. The result It is shown in [Table 2].

[0021]

[Table 1]

実施例	1	2	3
樹脂No.	樹脂1	樹脂2	樹脂3
施工作業性	○	○	○
曲げ強度 (kg/cm ²)	70.0	71.7	68.8
圧縮強度 (kg/cm ²)	110.0	130.0	117.4
たわみ量 (mm)	1.05	1.00	0.92
耐候性 * 1	○	○	○
耐久性 * 2	○	○	○
仕上り性外観	○	○	○

* 1 : サンシャインウエザオメーター 1000時間暴露
* 2 : タイヤ切り返し試験 (加重摩耗試験機)

[0022]

[Table 2]

比較例	1	2	3	4	5	6	7
樹脂No.	樹脂1	樹脂2	樹脂3	樹脂4	樹脂5	樹脂6	樹脂7
施工作業性	○	△	×-△	×	○	○	○
曲げ強度 (kg/cm ²)	68.0	65.0	52.0	27.7	69.8	20.3	71.0
圧縮強度 (kg/cm ²)	132.1	103.7	90.2	54.8	93.8	47.1	132.0
たわみ量 (mm)	0.79	1.19	0.85	2.48	1.07	1.04	0.75
耐候性 * 1	—	○	○	○	○	×-△	× f3-47g
耐久性 * 2	—	△	△	×	△	×	△
仕上り性外観	発泡	○	○	○	樹脂落ち 著しい	光沢 劣る	○

* 1 : サンシャインウエザオメーター 1000時間暴露
* 2 : タイヤ切り返し試験 (加重摩耗試験機)

[0023]Physical-properties intensity-measurement condition flexural strength: A part for crosshead speed 2mm/ 100 mm of Sepang compressive strength: A part for crosshead speed 2mm/ A compression area tire cutback examination of 40x40 mm (endurance) compression load : 30 kg/cm² torsion speed: — 4-rpm tire: — casting urethane resin number of 98 hardness JISA article cycles: — 100 cycle [Table 1] **Valuation-basis execution workability in [Table 2] (trowel workability)

O : — unusual — it carries out and the adhesion weatherability O:surface of adhesion x:aggregate is [**:aggregate / a trowel] slightly unusual to a trowel — it carries out and **:gloss fall x:gloss degradation, discoloration, and the chalking endurance O:surface are unusual — carry out and exfoliate from a **:surface exfoliation x:ground [0024]Although the result examples 1, 2, and 3 were molded considering aggregate, such as a living rock, as a paving material, the Plastic solid was excellent in flexural strength and compressive strength, and was good. [of execution workability, weatherability, and endurance] On the other hand, since the comparative example 1 had the high isocyanate group content, foaming produced it. Although the comparative examples 2 and 3 are excellent in weatherability, they are inferior in endurance and execution workability. Although the comparative example 4 is the

prepolymer which polymers-ized the hexamethylene di-isocyanate system prepolymer which has an isocyanurate ring by poly(oxypropylene)triol and polytetramethylene ether glycol, physical-properties intensity is low, endurance is also inferior and resin viscosity of workability is highly bad. Since the comparative example 5 has low solid content, resin omission is remarkable, and the surface strength reduction of a Plastic solid is accepted in connection with it. Although the comparative example 6 uses the independent prepolymer of a hexamethylene di-isocyanate system, physical-properties intensity is low and weatherability and endurance are also inferior. Although it is the epoxy resin currently used from the former, physical-properties intensity is high, but the comparative example 7 is inferior to weatherability, and inferior to design nature in discoloration and gloss degradation remarkably.

[0025]

[Effect of the Invention] Since viscosity and working life are suitable for the moisture curing type binding material of this invention, construction is easy, and since the hardened material has the outstanding weatherability and endurance, it comes out of it to employ efficiently the color which aggregate has over a long period of time. Since it excels also in shock resistance and water permeability, the paving material which furthermore contains the binding material and aggregate of this invention is suitably used as binders for water-permeable pavings, such as a promenade, a motor pool, and the poolside.

[Translation done.]